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# A density functional theory study of frequency-dependent polarizabilities and Van der Waals dispersion coefficients for polyatomic molecules

S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends

Department of Physical and Theoretical Chemistry, Vrije Universiteit,  
De Boelelaan 1083, 1081 HV, Amsterdam, The Netherlands

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A method for calculating frequency-dependent polarizabilities and Van der Waals dispersion coefficients, which scales favorably with the number of electrons, has been implemented in the Amsterdam Density Functional package. Time-dependent Density Functional Theory is used within the Adiabatic Local Density Approximation (ALDA). Contrary to earlier studies with this approximation, our implementation applies to arbitrary closed-shell molecular systems. Our results for the isotropic part of the Van der Waals dispersion energy are of comparable quality as those obtained in TDCHF calculations. The ALDA results for the relative anisotropy of the dipole dispersion energy compare favorably to TDCHF and MBPT results. Two semi-empirical ways to calculate the dispersion energy anisotropy are evaluated. Large bases which include diffuse functions are necessary for a good description of the frequency-dependent properties considered here. © 1995 American Institute of Physics.

## I. INTRODUCTION

In recent years there have been several Density Functional Theory (DFT) studies on the quality of static polarizabilities and hyperpolarizabilities. These are either finite field calculations<sup>1-4</sup> or an implementation of the coupled Kohn-Sham equations.<sup>5,6</sup>

To the best of our knowledge, all the calculations of frequency-dependent (hyper-)polarizabilities in DFT until now, have made use of time-dependent DFT in which the Adiabatic Local Density Approximation (ALDA) is used. However, these studies are either restricted to atomic systems<sup>7-10</sup> or to a single center expansion<sup>11</sup> which is unsuitable for general molecules. An alternative DFT method for calculating frequency-dependent response properties has been developed by Colwell *et al.*<sup>5</sup> No results have yet been reported.

The articles cited above show that the LDA results for static polarizabilities are good, though generally somewhat too high ( $\sim 5\%$ ). This is due to the fact that the LDA density falls off too slowly, which means that the deformability of the electron cloud becomes too high.

We are interested in frequency-dependent properties for two main reasons. The first reason is that there is an interesting link between Van der Waals dispersion coefficients and multipolar polarizabilities at imaginary frequencies.<sup>12,13</sup> This opens up a route to constructing the long range part of potential energy surfaces for Van der Waals complexes within DFT. The present day local and non-local functionals do not seem to give satisfactory results for such complexes in supermolecule calculations.<sup>14,15</sup>

For small molecules often satisfactory isotropic Van der Waals coefficients can be obtained with correlated *ab initio* methods such as many-body perturbation theory (MBPT),<sup>16</sup> but these methods are restricted to small molecules because of their unfavorable scaling behavior ( $N^m$ ,  $m \geq 5$ ). Our implementation provides a tractable alternative for medium-sized molecules, because it scales like  $N^3$ .

The second reason for our interest in frequency-dependent polarizabilities is the fact that much experimental work is done at non-zero frequency. Now, a more direct comparison with experiment becomes possible and an alternative is provided for frequency ranges which cannot be reached easily in an experiment.

## II. THE MODEL

After some pioneering works by, among others, Zangwill and Soven,<sup>7</sup> Ghosh and Deb,<sup>10</sup> Bartolotti,<sup>8</sup> and Stott and Zaremba,<sup>17</sup> the rigorous foundation for time-dependent DFT was given by Runge and Gross<sup>18</sup> who formulated a time-dependent version of the Kohn-Sham scheme.<sup>19,20</sup> References 21 and 22 provide excellent reviews of time-dependent DFT. In the following, we will basically follow these reviews.

The Fourier transforms of the first order change in the density  $\delta\rho(\mathbf{r},\omega)$ , and of a scalar time-dependent change in the external potential  $\delta v_{\text{ext}}(\mathbf{r},\omega)$  can be related by the full linear response function  $\chi(\mathbf{r},\mathbf{r}',\omega)$ :

$$\delta\rho(\mathbf{r},\omega) = \int d\mathbf{r}' \chi(\mathbf{r},\mathbf{r}',\omega) \delta v_{\text{ext}}(\mathbf{r}',\omega). \quad (1)$$

However, it is very difficult to find good approximations for this linear response function, since it requires in principle the knowledge of all exact eigenfunctions and excitation energies of the system. The time-dependent DFT alternative is to use the response function  $\chi_s(\mathbf{r},\mathbf{r}',\omega)$  of the non-interacting Kohn-Sham system, in combination with an effective or screened potential  $\delta v_{\text{eff}}(\mathbf{r},\omega)$ :

$$\delta\rho(\mathbf{r},\omega) = \int d\mathbf{r}' \chi_s(\mathbf{r},\mathbf{r}',\omega) \delta v_{\text{eff}}(\mathbf{r}',\omega). \quad (2)$$

This response function requires the knowledge of the occupied and virtual Kohn-Sham orbitals  $\{\phi\}$  and energies  $\{\epsilon\}$ , as well as the occupation numbers  $n$ , which are all obtained in a standard DFT calculation:

$$\chi_s(\mathbf{r}, \mathbf{r}', \omega) = \sum_i^{\text{occ.}} \sum_m^{\text{virt.}} n_i \phi_i(\mathbf{r}) \phi_m(\mathbf{r}) \phi_m(\mathbf{r}') \phi_i(\mathbf{r}') \times \left( \frac{1}{(\epsilon_i - \epsilon_m) + \omega} + \frac{1}{(\epsilon_i - \epsilon_m) - \omega} \right). \quad (3)$$

The change in the effective potential  $\delta v_{\text{eff}}(\mathbf{r}, \omega)$ , which depends upon the density change  $\delta \rho(\mathbf{r}, \omega)$  is given by:

$$\delta v_{\text{eff}}(\mathbf{r}, \omega) = \delta v_{\text{ext}}(\mathbf{r}, \omega) + \int d\mathbf{r}' \frac{\delta \rho(\mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} + \delta v_{\text{xc}}(\mathbf{r}, \omega). \quad (4)$$

The change in the exchange correlation potential is given in terms of the Fourier transform of the so-called exchange correlation kernel  $f_{\text{xc}}(\mathbf{r}, \mathbf{r}'; \omega)$ :

$$\delta v_{\text{xc}}(\mathbf{r}, \omega) = \int d\mathbf{r}' f_{\text{xc}}(\mathbf{r}, \mathbf{r}'; \omega) \delta \rho(\mathbf{r}', \omega). \quad (5)$$

The exchange correlation kernel is the functional derivative of the exchange correlation potential with respect to the time-dependent density. In the ALDA this kernel is local, both in space and time. Most applications of time-dependent DFT have used the ALDA so far,<sup>7,9,11,23</sup>

$$f_{\text{xc}}^{\text{ALDA}}(\mathbf{r}, \mathbf{r}'; \omega) = \delta(\mathbf{r} - \mathbf{r}') \frac{d^2}{d\rho^2} [\rho \epsilon_{\text{xc}}(\rho)]|_{\rho=\rho_0(\mathbf{r})}, \quad (6)$$

where  $\rho_0(\mathbf{r})$  is the converged SCF density. The Vosko-Wilk-Nusair<sup>24</sup> parametrization for the exchange correlation energy density  $\epsilon_{\text{xc}}$  of a homogeneous electron gas is used. Although the ALDA can only be expected to be a good approximation for slow time-dependent processes, it appears to work well even outside this region.<sup>7</sup>

A frequency-dependent extension, based upon a Padé-type interpolation between high and low frequency limits of the homogeneous electron gas, has been derived by Gross and Kohn.<sup>25</sup> However, the main deficiency of the ALDA seems to be in the spatial part rather than in the lack of frequency-dependence.<sup>22,9,7</sup>

The set of equations (2), (3), (4) and (5) must be solved self-consistently. After this has been done, the frequency-dependent polarizability  $\alpha(\omega)$  is directly available, for a density change  $\delta \rho_i(\mathbf{r}, \omega)$  due to an external potential  $\delta v_{\text{ext},i}(\mathbf{r}, t) = E r_i \cos(\omega t)$ :

$$\alpha_{ij}(\omega) = -\frac{2}{E} \int d\mathbf{r} \delta \rho_i(\mathbf{r}, \omega) r_j, \quad (7)$$

where  $i$  and  $j$  denote the Cartesian directions  $x, y, z$ . There is an interesting relation between multipolar polarizabilities at imaginary frequencies and Van der Waals dispersion coefficients.<sup>12,26,13</sup> The most general formulation<sup>13,27</sup> involves a double spherical harmonics expansion.

In the present paper, we will restrict ourselves to the  $R^{-6}$  term of the dispersion interaction energy between two linear molecules, for which expressions are given in References 28 and 29. The  $R^{-6}$  term involves dipole polarizabilities only. It is governed by the isotropic coefficient  $C_6$  and by two anisotropic coefficients:  $C'_6$  and  $C''_6$ , which control the orientation-dependent part of the long-range interaction. The average polarizability  $\alpha$  and the anisotropy  $\kappa$  are de-

fined with respect to the polarizability tensor components parallel and perpendicular to the main molecular symmetry axis:

$$\alpha = \frac{\alpha_{\parallel} + 2\alpha_{\perp}}{3}, \quad (8)$$

$$\kappa = \alpha_{\parallel} - \alpha_{\perp}. \quad (9)$$

The dispersion coefficients between linear molecules  $A$  and  $B$  are related to these properties at imaginary frequencies, by the following integral relations<sup>28</sup> (Hartree atomic units are used throughout the article, unless otherwise stated):

$$C_6(A, B) = \frac{3}{\pi} \int_0^{\infty} \alpha_A(i\omega) \alpha_B(i\omega) d\omega, \quad (10)$$

$$C'_6(A, B) = \frac{1}{\pi} \int_0^{\infty} \kappa_A(i\omega) \alpha_B(i\omega) d\omega, \quad (11)$$

$$C''_6(A, B) = \frac{1}{3\pi} \int_0^{\infty} \kappa_A(i\omega) \kappa_B(i\omega) d\omega. \quad (12)$$

These equations can also be used for the symmetrical top molecules  $\text{NH}_3$ ,  $\text{C}_2\text{H}_6$  and  $\text{c-C}_3\text{H}_6$ .<sup>29</sup> We further use the relative anisotropies  $\Gamma(A, B)$  and  $\Delta(A, B)$ , defined by<sup>30</sup>:

$$\Gamma(A, B) = \frac{C'_6(A, B)}{C_6(A, B)}, \quad (13)$$

$$\Delta(A, B) = \frac{C''_6(A, B)}{C_6(A, B)}. \quad (14)$$

### III. IMPLEMENTATION

The ADF program (References 31–35) makes use of STO basis and fit sets. Further characteristics include the use of an accurate numerical integration scheme<sup>33,34</sup> and the possibility to apply a frozen core approximation.

The fit set  $\{f_i\}$  employed in ADF is used to approximate the first order density change by:

$$\delta \rho(\mathbf{r}, \omega) = \sum_i^{\text{nfit}} C_i(\omega) f_i(\mathbf{r}), \quad (15)$$

where the coefficients  $C_i(\omega)$  are real numbers. This enables one to do the integration involved in the Coulomb term of equation (4) analytically. Because of the local form of the exchange correlation kernel  $f_{\text{xc}}$ , the integration in equation (5) is trivial and one obtains:

$$\begin{aligned} \delta v_{\text{eff}}(\mathbf{r}, \omega) &= \delta v_{\text{ext}}(\mathbf{r}, \omega) + \sum_i^{\text{nfit}} C_i(\omega) \left( \int d^3\mathbf{r}' \frac{f_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right. \\ &\quad \left. + f_i(\mathbf{r}) \frac{d^2}{d\rho^2} [\rho \epsilon_{\text{xc}}(\rho)]|_{\rho=\rho_0(\mathbf{r})} \right) \\ &\equiv \delta v_{\text{ext}}(\mathbf{r}, \omega) + v_{\text{ind}}(\mathbf{r}, \omega). \end{aligned} \quad (16)$$

The Coulomb and exchange correlation term are combined into an induced potential  $v_{\text{ind}}$  which is known in all the integration points of the numerical integration grid.

Substituting equations (16) and (3) into equation (2) yields:

$$\delta\rho(\mathbf{r},\omega)=\sum_i^{\text{occ.}}\sum_m^{\text{virt.}}n_i\phi_i(\mathbf{r})\phi_m(\mathbf{r})\left(\frac{1}{(\varepsilon_i-\varepsilon_m)+\omega}+\frac{1}{(\varepsilon_i-\varepsilon_m)-\omega}\right)\int d^3\mathbf{r}'\phi_i(\mathbf{r}')\phi_m(\mathbf{r}')\times[\delta v_{\text{ext}}(\mathbf{r}',\omega)+v_{\text{ind}}(\mathbf{r}',\omega)]. \quad (17)$$

For real orbitals  $\phi$  the density change is given by:

$$\delta\rho(\mathbf{r},\omega)=\sum_i^{\text{occ.}}\sum_m^{\text{virt.}}n_iP_{im}(\omega)\phi_i(\mathbf{r})\phi_m(\mathbf{r}). \quad (18)$$

Combining the last two equations gives

$$P_{im}(\omega)=\left(\frac{1}{(\varepsilon_i-\varepsilon_m)+\omega}+\frac{1}{(\varepsilon_i-\varepsilon_m)-\omega}\right)\times\int d^3\mathbf{r}'\phi_i(\mathbf{r}')\phi_m(\mathbf{r}')\times[\delta v_{\text{ext}}(\mathbf{r}',\omega)+v_{\text{ind}}(\mathbf{r}',\omega)]. \quad (19)$$

The coefficients  $\{P_{im}\}$  are found by a self-consistent procedure. Starting with the uncoupled case ( $v_{\text{ind}}(\mathbf{r},\omega)=0$ ), one obtains an initial set  $\{P_{im}\}$ . Then the density is fitted in order to obtain the coefficients  $\{C_i\}$ . These result in a new potential  $v_{\text{ind}}$ , which results in new coefficients  $\{P_{im}\}$ . This is repeated until the change in the coefficients becomes negligible. In order to speed up the convergence, the Direct Inversion in the Iterative Subspace (DIIS) method originating from Pulay<sup>36,37</sup> is used. The expensive steps in the procedure are the integrations of equation (19), which are evaluated with an accurate numerical integration procedure,<sup>33,34</sup> and the density fit.<sup>31</sup> The use of atom-centered basis functions allows to break up the density in one- and two-center charge distributions. A least squares fit of each atom-atom charge distribution is performed with fitting functions on the two atoms. This procedure avoids the increase of the dimension of the fitting problems with system size.

#### IV. DESCRIPTION OF BASIS SETS AND PARAMETERS IN THE CALCULATIONS

For first row atoms, the largest standard STO basis set in ADF is a triple zeta s, p basis to which a 3d and a 4f polarization function are added. For the H-atom, this basis consists of a triple zeta s basis, extended with a 2p and 3d polarization function. This basis will be called 3Z2P in this paper. For the correct description of such sensitive properties as polarizabilities, it is mandatory to add diffuse functions to the basis. Our first extension of the 3Z2P basis, which we will denote by 3Z2P\*, adds the diffuse s, p and d functions with exponents recommended by Zeiss *et al.*<sup>38,4</sup> in the case of the H, F, N, O and C atoms. For the rare gas atoms we follow Colwell *et al.*,<sup>5</sup> by adding diffuse s, p and d functions with exponents which were one third of the smallest exponents used in the standard 3Z2P basis.

Because the results with this basis are still not close enough to the basis set limit, we use a basis 3Z2P\*\*, in

which each diffuse function of the 3Z2P\* basis was replaced by two diffuse functions, one with a lower and one with a higher exponent.

After some tests with even larger basis sets and by comparison to basis set free methods (see later), the results with the 3Z2P\*\* basis were found to be close to the basis set limit, being still slightly too low. We estimate our results to be within 3% of the basis set limit. We have employed the 3Z2P\*\* basis for all calculations in this work, unless otherwise stated.

The influence of the fit set was minimized by taking almost saturated fit sets, without letting the overlap between different fit functions become too large.

The accuracy of the numerical integration was set such that several standard integrals are evaluated with at least five digit accuracy, enough to neglect remaining errors.

The integrals in equations (10), (11) and (12) are solved by the twenty point Gauss–Chebyshev quadrature described in Reference 13. The error made by using this approximation is smaller than errors caused by basis set or fit set effects.

In most tables, the estimated computational accuracy is given. These estimates do not include basis set effects. They were made by comparing to results with somewhat smaller fit sets.

The core of all atoms except He and H was kept frozen. The outermost frozen shell was 1s for Ne, N, O, F, C, 2p for Ar and 3d for Kr. The effect of the frozen core for the polarizability of the rare gases was 1.1% for Ar and less than 0.2% for the other atoms. The effect of the frozen core approximation on molecular polarizabilities is expected to be smaller in the relative sense.

The experimental equilibrium geometries were used for all our calculations.<sup>39</sup>

The number of iterations needed in order to solve the set of equations (2), (3), (4) and (5) for one frequency, varies between 3 and 10. A few hours on an IBM RS6000/550 workstation are needed to calculate the full polarizability tensor for c-C<sub>3</sub>H<sub>6</sub> at ten imaginary frequencies, with the largest basis and fit sets and the biggest numerical integration grid we used. These numbers should give an impression of the efficiency of the implementation.

#### V. COMPARISON WITH OTHER THEORETICAL METHODS

##### A. Static and frequency-dependent polarizabilities

As a first test of our implementation, we reproduced our finite field calculations on polarizabilities for several systems. The relative deviations found lie between 0.002 for H<sub>2</sub>O and  $3 \cdot 10^{-6}$  for Ne. This is satisfactory because in the case of H<sub>2</sub>O the finite field result still contains some higher order effects.

We calculated the frequency-dependent polarizabilities of several rare gas atoms, in order to assess the quality of our basis sets and to compare our results to those obtained by Senatore and Subbaswamy,<sup>9</sup> whose ALDA solution method is basis set free. They fitted the experimental data<sup>40</sup> and their own result for the frequency-dependent polarizability of the rare gases, with the formula

TABLE I. Comparison of the frequency-dependence of the polarizability of rare gas atoms with basis set free ALDA results (Reference 9) and with experiment. The results are fitted according to equation (20).

Atom		He	Ne	Ar	Kr
This work 3Z2P	$\alpha_0$	1.65	2.28	9.32	13.32
This work 3Z2P*	$\alpha_0$	1.65	2.77	11.07	15.68
This work 3Z2P**	$\alpha_0$	1.65	3.02	11.94	17.67
PZ ALDA <sup>a</sup>	$\alpha_0$	1.66	3.05	12.01	18.02
Other LDA <sup>d</sup>	$\alpha_0$		2.99, <sup>b</sup> 3.15 <sup>c</sup>	11.80, <sup>b</sup> 12.48 <sup>c</sup>	17.70, <sup>b</sup> 18.86 <sup>c</sup>
Expt. <sup>e</sup>	$\alpha_0$	1.38	2.67	11.07	16.74
This work 3Z2P	$C_2$	1.40	0.60	2.02	1.89
This work 3Z2P*	$C_2$	1.39	1.44	3.03	3.34
This work 3Z2P**	$C_2$	1.46	1.49	3.07	4.02
PZ ALDA <sup>a</sup>	$C_2$	1.49	1.49	3.13	4.10
Expt. <sup>e</sup>	$C_2$	1.16	1.11	2.60	3.61

<sup>a</sup>Numerical ALDA results (Ref. 9) according to the Perdew Zunger (Ref. 42) parametrization of the homogeneous electron gas exchange correlation functional.

<sup>b</sup>Gunnarsson Lundqvist representation of exchange correlation potential (Ref. 44).

<sup>c</sup>Ceperley Alder (Ref. 41) exchange correlation data for the homogeneous electron gas, as used by Mahan and Subbaswamy (Ref. 43).

<sup>d</sup>Reference 43.

<sup>e</sup>Reference 40.

$$\alpha(\omega) = \alpha_0(1 + C_2\omega^2). \quad (20)$$

The results are given in Table I. In this table, the differences between our results and those obtained by Senatore and Subbaswamy<sup>9</sup> are small. Our results are clearly closer to Senatore and Subbaswamy's results than to the experimental values, being always in between the two. Taking even bigger basis sets does not change the results significantly. From this fact and from the small differences between our results and those obtained by Senatore and Subbaswamy, we conclude that our basis and fit sets are of high quality and that our results are close to the basis set limit. The remaining differences can partially be attributed to the different parametrizations used for the numerical Ceperley and Alder electron gas results,<sup>41</sup> because Senatore and Subbaswamy use the Perdew–Zunger parametrization,<sup>42</sup> where we employ the Vosko–Wilk–Nusair<sup>24</sup> parametrization.

In Table I also some LDA results for  $\alpha_0$  using different methods and different parametrizations for the exchange correlation potential are reported. The results show considerable variation, which puts the (small) differences which we obtain with respect to Reference 9 in perspective.

The behavior of the frequency-dependent polarizability of Kr at imaginary frequencies is shown in Figure 1. Our result is compared to the ALDA result given on page 111 of Reference 43, where the Gunnarsson–Lundqvist<sup>44</sup> expression for the exchange correlation potential has apparently been used.

The good agreement of the zero frequency result is somewhat fortuitous, but the figure does show that the description of the frequency-dependence agrees very well too. For Ne and Ar we find similar results.

In Table II, we compare our results for the static polarizability of several molecules with experimental and theoretical results. These results can be used to estimate the reliability of the dispersion coefficients which will be presented in

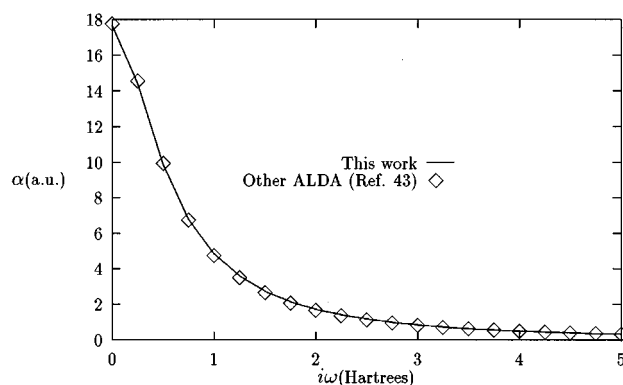


FIG. 1. The polarizability of Kr at imaginary frequencies.

the remainder of the article. In agreement with previous work,<sup>1–4</sup> we note that the average polarizability  $\alpha_0$  is generally satisfactory, but somewhat too high. The anisotropies  $\kappa_0$  do not show clear systematic deviation. They are of similar quality as  $\alpha_0$ , except for  $\text{NH}_3$ , where there is considerable spread in the results anyway.

The reference values in Table II and the rest of this article are reliable constrained Dipole Oscillator Strength Distribution (DOSD) results, obtained through the use of experimental and theoretical dipole oscillator strength data and a system of quantum mechanical sum rule constraints.

## B. Isotropic dispersion coefficients

In this paper we are primarily interested in the quality of  $C_6$  Van der Waals dispersion coefficients for medium-sized molecules, calculated within the ALDA. The study of Bartolotti<sup>8</sup> for the rare gases was promising in this respect.

TABLE II. Static polarizabilities.

Mol.	Comp.	Experiment/ DOSD	Hohm <sup>g</sup>	This work	Other LDA results
H <sub>2</sub>	$\alpha_0$	5.433; <sup>c</sup> 5.53 <sup>a</sup>	5.43	6.10	6.13 <sup>f</sup>
H <sub>2</sub>	$\kappa_0$	2.042; <sup>c</sup> 2.12 <sup>a</sup>	2.04	2.15	2.09 <sup>f</sup>
N <sub>2</sub> O	$\alpha_0$	19.77; <sup>b</sup> 20.3 <sup>a</sup>	19.70	19.80	
N <sub>2</sub> O	$\kappa_0$	19.10; <sup>b</sup> 20.0 <sup>a</sup>	19.10	18.44	
CO <sub>2</sub>	$\alpha_0$	17.48; <sup>b</sup> 17.75 <sup>a</sup>	17.50	17.74	17.80 <sup>e</sup>
CO <sub>2</sub>	$\kappa_0$	13.70; <sup>b</sup> 14.2 <sup>a</sup>	13.72	13.61	13.96 <sup>e</sup>
NH <sub>3</sub>	$\alpha_0$	15.0 <sup>a</sup>	14.56	15.62	15.57; <sup>c</sup> 15.44 <sup>f</sup>
NH <sub>3</sub>	$\kappa_0$	1.94 <sup>a</sup>	1.04	3.08	2.67; <sup>c</sup> 1.85 <sup>f</sup>
C <sub>2</sub> H <sub>6</sub>	$\alpha_0$	30.2 <sup>a</sup>	29.54	30.70	
C <sub>2</sub> H <sub>6</sub>	$\kappa_0$	5.2 <sup>a</sup>	4.19	4.32	
c-C <sub>3</sub> H <sub>6</sub>	$\alpha_0$	38.0 <sup>a</sup>	37.30	39.25	
c-C <sub>3</sub> H <sub>6</sub>	$\kappa_0$	-5.4 <sup>a</sup>	-4.79	-5.09	
N <sub>2</sub>	$\alpha_0$	11.74; <sup>c</sup> 11.74 <sup>b</sup>		12.30	11.84 <sup>f</sup>
N <sub>2</sub>	$\kappa_0$	4.45 <sup>b</sup>		4.68	5.36 <sup>f</sup>
CO	$\alpha_0$	13.08 <sup>d</sup>		13.68	13.41 <sup>f</sup>
CO	$\kappa_0$	3.567 <sup>d</sup>		3.30	3.90 <sup>f</sup>

<sup>a</sup>Reference 49 measurements at 6328 Å.

<sup>b</sup>Reference 50.

<sup>c</sup>Reference 45.

<sup>d</sup>Reference 30.

<sup>e</sup>Reference 1.

<sup>f</sup>Reference 2.

<sup>g</sup>Reference 29.

TABLE III. Isotropic dispersion coefficients  $C_6(A,B)$ . The computational accuracy for our results is estimated to be 1%.

A	B	MBPT	TDCHF	This work	DOSD
He	He	1.431 <sup>c</sup>	1.375 <sup>c</sup>	1.82	1.458 <sup>g</sup>
He	Ne	3.0712 <sup>a</sup>	2.697 <sup>c</sup>	3.60	3.029 <sup>g</sup>
He	Ar	9.5667 <sup>a</sup>		11.2	9.538 <sup>g</sup>
He	Kr	13.652 <sup>a</sup>		15.4	13.40 <sup>g</sup>
Ne	Ne	6.5527 <sup>a</sup>	5.392; <sup>f</sup> 5.5136 <sup>a</sup>	7.26	6.383 <sup>g</sup>
Ne	Ar	19.753 <sup>a</sup>	17.641 <sup>a</sup>	21.8	19.50 <sup>g</sup>
Ne	Kr	28.009 <sup>a</sup>	24.802 <sup>a</sup>	29.9	27.30 <sup>g</sup>
Ar	Ar	64.543 <sup>a</sup>	61.833 <sup>a</sup>	69.9	64.30 <sup>g</sup>
Ar	Kr	93.161 <sup>a</sup>	88.563 <sup>a</sup>	97.1	91.13 <sup>g</sup>
Kr	Kr	135.08 <sup>a</sup>	127.41 <sup>a</sup>	135	129.6 <sup>g</sup>
H <sub>2</sub>	H <sub>2</sub>	12.62 <sup>c</sup>	12.30 <sup>c</sup>	14.3	12.09 <sup>j</sup>
H <sub>2</sub>	N <sub>2</sub>	30.54 <sup>c</sup>	29.28 <sup>f</sup>	32.8	29.46 <sup>i</sup>
H <sub>2</sub> O	H <sub>2</sub> O	46.443; <sup>b</sup> 47.623; <sup>b</sup> 48.794 <sup>b</sup>	39.437 <sup>b</sup>	50.1	45.37 <sup>h</sup>
H <sub>2</sub> O	N <sub>2</sub>			62.2	57.68 <sup>h</sup>
H <sub>2</sub> O	NH <sub>3</sub>			68.6	63.41 <sup>h</sup>
NH <sub>3</sub>	NH <sub>3</sub>			94.4	89.08 <sup>h</sup>
NH <sub>3</sub>	Ar	75.216; <sup>b</sup> 78.143 <sup>b</sup>	69.170 <sup>b</sup>	81.0	
NH <sub>3</sub>	N <sub>2</sub>			85.0	80.48 <sup>h</sup>
N <sub>2</sub>	N <sub>2</sub>	75.63 <sup>c</sup>	71.46 <sup>f</sup>	77.2	73.43 <sup>i</sup>
Ne	N <sub>2</sub>	21.525; <sup>a</sup> 21.75 <sup>c</sup>	18.88; <sup>f</sup> 19.07 <sup>c</sup>	23.1	20.97 <sup>i</sup>
Ar	N <sub>2</sub>	69.843 <sup>a</sup>		73.5	68.69 <sup>i</sup>
Kr	N <sub>2</sub>	100.67 <sup>a</sup>		102	97.28 <sup>i</sup>
Ne	HF	11.502 <sup>a</sup>		12.7	10.87 <sup>g</sup>
Ar	HF	36.334 <sup>a</sup>		39.9	34.73 <sup>g</sup>
Kr	HF	52.053 <sup>a</sup>		55.2	49.00 <sup>g</sup>
Ne	CO	23.075; <sup>a</sup> 22.047; <sup>c</sup> 23.32 <sup>c</sup>	19.24 <sup>c</sup>	23.8	21.87 <sup>j</sup>
Ar	CO	75.806; <sup>a</sup> 73.597 <sup>c</sup>		76.5	72.26 <sup>j</sup>
Kr	CO	109.63; <sup>a</sup> 106.43 <sup>c</sup>		106	102.5 <sup>j</sup>
CO	CO	89.14 <sup>c</sup>	73.96 <sup>c</sup>	83.8	81.31 <sup>j</sup>
CO	N <sub>2</sub>	82.01 <sup>c</sup>	72.65 <sup>c</sup>	80.4	77.21 <sup>j</sup>
CO <sub>2</sub>	CO <sub>2</sub>			161	158.7 <sup>k</sup>
N <sub>2</sub> O	N <sub>2</sub> O			186	184.9 <sup>h</sup>
C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub>			397	381.8 <sup>l</sup>

<sup>a</sup>Reference 51.<sup>g</sup>Reference 54.<sup>b</sup>Reference 52.<sup>h</sup>Reference 55.<sup>c</sup>Reference 13.<sup>i</sup>Reference 45.<sup>d</sup>Reference 53.<sup>j</sup>Reference 30.<sup>e</sup>Reference 46.<sup>k</sup>Reference 56.<sup>f</sup>Reference 27.<sup>l</sup>Reference 57.

In Table III our values with basis set 3Z2P\*\* are compared to time-dependent coupled Hartree Fock (TDCHF) and MBPT results close to the basis set limits. The reference values are the DOSD results.

A few important trends can be derived from Table III.

- (1) The ALDA results for frequency-dependent polarizabilities and isotropic  $C_6$  Van der Waals dispersion coefficients are generally too high. This was to be expected, since the aforementioned studies on static polarizabilities show the same trend.
- (2) The ALDA results involving He or H<sub>2</sub>, or other small systems are relatively poor. They are approximately 15% to 20% too high. Going towards bigger systems, the results tend to improve (1% to 10% too high). This is interesting, because MBPT calculations are not feasible anymore for larger systems. The ALDA offers a parameter-free alternative.
- (3) The ALDA results are of similar quality as the TDCHF

TABLE IV. Relative anisotropy in dispersion coefficients  $\Gamma(A,B)$ .

A-B	DOSD <sup>a</sup>	TDCHF <sup>b</sup>	MBPT <sup>b</sup>	MBPT <sup>c</sup>	This work
CO-CO	0.0940	0.0854	0.1245		0.0850
CO-H <sub>2</sub>	0.0949	0.0872	0.1264		0.0861
H <sub>2</sub> -CO	0.0976	0.0993	0.1057		0.0950
CO-N <sub>2</sub>	0.0939	0.0854	0.1238		0.0848
N <sub>2</sub> -CO	0.1077	0.1185	0.1306		0.1092
H <sub>2</sub> -H <sub>2</sub>	0.1006				0.0962
H <sub>2</sub> -N <sub>2</sub>	0.1109				0.0940
N <sub>2</sub> -H <sub>2</sub>	0.0966				0.1119
N <sub>2</sub> -N <sub>2</sub>	0.1068				0.1084
CO-He	0.0930	0.187	0.270	0.1036	0.0842
CO-Ne	0.0916	0.182	0.265	0.1013	0.0824
CO-Ar	0.0942			0.1067	0.0852
CO-Kr	0.0943			0.1077	0.0855
H <sub>2</sub> -He	0.0924				0.0906
H <sub>2</sub> -Ne	0.0901				0.0882
H <sub>2</sub> -Ar	0.0971				0.0934
H <sub>2</sub> -Kr	0.0986				0.0945
N <sub>2</sub> -He	0.1027				0.1063
N <sub>2</sub> -Ne	0.0999				0.1032
N <sub>2</sub> -Ar	0.1074				0.1090
N <sub>2</sub> -Kr	0.1087				0.1101

<sup>a</sup>References 30 and 45.<sup>b</sup>Reference 13.<sup>c</sup>Reference 46.

results. They are slightly worse for small systems and somewhat better for larger systems.

### C. Anisotropic dispersion coefficients

An interesting application of the presented theory is the calculation of the anisotropic Van der Waals dispersion coefficients  $C'_6$  and  $C''_6$  of Equations (11) and (12). Due to the scarceness of experimental data on the polarizability anisotropy, accurate constrained DOSD (References 30,45) calculations are available for a few small molecules only. *Ab initio* TDCHF and MBPT calculations are possible, but not uniformly reliable as shown by Tables IV and V, which contain DOSD data from References 30 and 45.

We have added our own ALDA results to these tables. The relative anisotropies obtained with the ALDA are at least of comparable quality as the TDCHF and MBPT results and sometimes markedly superior (the TDCHF results for CO-He and CO-Ne in Table IV provide examples). It has to be remarked that the MBPT calculations of Reference 46 clearly improve earlier MBPT result of Reference 13. Hettrema states

TABLE V. Relative anisotropy in dispersion coefficients  $\Delta(A,B)$ .

A-B	DOSD <sup>a</sup>	TDCHF <sup>b</sup>	MBPT <sup>b</sup>	This work
CO-CO	0.0090	0.0075	0.0159	0.007 39
CO-H <sub>2</sub>	0.0094	0.0089	0.0137	0.008 33
CO-N <sub>2</sub>	0.0103	0.0105	0.0166	0.009 49
H <sub>2</sub> -H <sub>2</sub>	0.0108			0.009 70
H <sub>2</sub> -N <sub>2</sub>	0.0114			0.010 98
N <sub>2</sub> -N <sub>2</sub>	0.0121			0.012 25

<sup>a</sup>References 30 and 45.<sup>b</sup>Reference 13.

in his thesis<sup>16</sup> that the MBPT relative anisotropies of N<sub>2</sub> with the rare gases which he obtains, are roughly 35% too low. He concludes that his MBPT approach is not sufficient to deal with the strong electron correlation associated with the triple bonds in N<sub>2</sub> and CO. Maybe the most important result from Tables IV and V is that the ALDA results never differ from the accurate DOSD results by more than 18% (in the case of CO-CO, in Table V). The average deviation from the DOSD values is about 6% in Table IV and about 9% in Table V.

We conclude that at present, the ALDA method is the most reliable method for calculating anisotropic dispersion interaction coefficients for molecules for which insufficient accurate experimental data exist in order to perform a DOSD calculation. This conclusion is supported by the fact that LDA predicts the static polarizability anisotropy better than Hartree Fock calculations do.<sup>1</sup>

## VI. EVALUATION OF TWO SEMI-EMPIRICAL METHODS

In an interesting article, Hohm<sup>29</sup> recently calculated anisotropic dispersion coefficients for several molecules by two semi-empirical methods. In the first place he used the two traditional approximate formulas, which involve some mean excitation energy  $\bar{\omega}_{AB}$  and the static polarizability tensor:

$$C'_6(A,B) \approx \frac{\bar{\omega}_{AB}}{2} \kappa^A(0) \alpha^B(0), \quad (21)$$

$$C''_6(A,B) \approx \frac{\bar{\omega}_{AB}}{6} \kappa^A(0) \kappa^B(0). \quad (22)$$

Contrary to Hohm, we use the factor  $\frac{1}{6}$  in equation (22), in agreement with Reference 47. Hohm's own approach is to fit the average polarizability and the polarizability anisotropy to functions of the form:

$$\alpha(\omega) = \frac{1}{3} \left( \frac{f_{\parallel}}{\omega_{\parallel}^2 - \omega^2} + \frac{2f_{\perp}}{\omega_{\perp}^2 - \omega^2} \right), \quad (23)$$

$$\kappa(\omega) = \frac{f_{\parallel}}{\omega_{\parallel}^2 - \omega^2} - \frac{f_{\perp}}{\omega_{\perp}^2 - \omega^2}, \quad (24)$$

and to perform the integrations of equations (10), (11) and (12). The differences he found between these two semi-empirical approaches are quite substantial. Sometimes discrepancies of an order of magnitude or sign differences were encountered. Hohm expresses no clear preference for either method. As we have shown the validity of our approach in the beginning of the article, we can now use our method to compare the semi-empirical values given by Hohm to our own values and to discuss the peculiarities of the semi-empirical approaches.

In Tables VI, VII, and VIII, our results are compared to the results given by Hohm. In the first rows of these tables, our values are given in bold face.

Considering the isotropic dispersion coefficients  $C_6$  in Table VI, there is qualitative agreement between the different methods. Hohm's semi-empirical method yields values (in the second row) which are too low compared to the benchmark theoretical (DOSD) values in the third row, while our

TABLE VI. Isotropic dispersion coefficients  $C_6(A,B)$ . The computational accuracy in our results (first row, bold faced) is estimated to be 1%. The second row gives Hohm's results, according to equations (10) and (23). The third row gives accurate theoretical values, where available. Except for H<sub>2</sub>-H<sub>2</sub> these are DOSD values. The results in round brackets were obtained by a semi-empirical mixture rule (Ref. 29).

	H <sub>2</sub>	N <sub>2</sub> O	CO <sub>2</sub>	NH <sub>3</sub>	C <sub>2</sub> H <sub>6</sub>	c-C <sub>3</sub> H <sub>6</sub>
H <sub>2</sub>	<b>14.3</b>	<b>51.1</b>	<b>47.3</b>	<b>36.7</b>	<b>75.3</b>	<b>95.36</b>
	11.051	43.81	40.24	32.90	63.46	79.60
	12.058 <sup>a</sup>	46.97 <sup>b</sup>	43.33 <sup>c</sup>	32.78 <sup>b</sup>	(67.82)	...
N <sub>2</sub> O		<b>186.0</b>	<b>173.0</b>	<b>132.1</b>	<b>271.0</b>	<b>343.31</b>
		168.02	154.54	126.79	242.08	303.87
		184.9 <sup>b</sup>	(171.15)	128.1 <sup>b</sup>	(265.43)	...
CO <sub>2</sub>			<b>161.1</b>	<b>122.6</b>	<b>251.5</b>	<b>318.68</b>
			142.23	116.71	222.45	279.21
			158.7 <sup>c</sup>	(118.26)	(245.24)	...
NH <sub>3</sub>				<b>94.4</b>	<b>193.6</b>	<b>245.38</b>
				96.00	182.02	228.60
				89.08 <sup>b</sup>	(184.39)	...
C <sub>2</sub> H <sub>6</sub>					<b>397.4</b>	<b>503.5</b>
					350.22	439.55
					381.8 <sup>d</sup>	...
c-C <sub>3</sub> H <sub>6</sub>						<b>638.0</b>
						551.26
						...

<sup>a</sup>Reference 28.

<sup>b</sup>Reference 55.

<sup>c</sup>Reference 56.

<sup>d</sup>Reference 57.

results are a bit too high. Both Hohm's method and the mixture rule,<sup>29</sup> which was used to calculate the values in parentheses, provide reasonable results.

In Table VII results for the anisotropic dispersion coefficient  $C'_6$  are given. The second row gives Hohm's own

TABLE VII. Anisotropic dispersion coefficients  $C'_6(A,B)$ . The results of this work are given in the first row. The second row gives the results corresponding to equations (11), (23) and (24), while the third row corresponds to equation (21). For H<sub>2</sub> an accurate theoretical value has been given in the fourth row (Ref. 28). The computational accuracy for our results is estimated to be 5% for NH<sub>3</sub>, 3% for c-C<sub>3</sub>H<sub>6</sub>, and 2% for the other molecules.

	H <sub>2</sub>	N <sub>2</sub> O	CO <sub>2</sub>	NH <sub>3</sub>	C <sub>2</sub> H <sub>6</sub>	c-C <sub>3</sub> H <sub>6</sub>
H <sub>2</sub>	<b>1.39</b>	<b>4.83</b>	<b>4.44</b>	<b>3.53</b>	<b>7.24</b>	<b>9.17</b>
	1.22	4.59	4.20	3.42	6.72	8.42
	1.43	5.73	5.12	4.07	7.79	10.72
	1.219	...	...	...	...	...
N <sub>2</sub> O	<b>12.7</b>	<b>44.3</b>	<b>40.9</b>	<b>32.2</b>	<b>66.1</b>	<b>83.79</b>
	8.69	31.50	28.55	22.90	47.31	59.18
	14.78	59.79	53.46	42.25	80.47	111.79
CO <sub>2</sub>	<b>9.95</b>	<b>34.9</b>	<b>32.3</b>	<b>25.3</b>	<b>52.0</b>	<b>65.88</b>
	6.82	24.92	22.65	18.21	37.22	46.56
	10.68	43.23	38.65	30.54	58.14	80.82
NH <sub>3</sub>	<b>0.45</b>	<b>1.22</b>	<b>1.03</b>	<b>1.08</b>	<b>2.10</b>	<b>2.69</b>
	-4.86	-20.14	-18.91	-15.89	-27.45	-34.58
	0.77	3.12	2.79	2.21	4.21	5.83
C <sub>2</sub> H <sub>6</sub>	<b>2.7</b>	<b>9.4</b>	<b>8.6</b>	<b>6.9</b>	<b>14.1</b>	<b>17.90</b>
	-1.07	-5.21	-5.10	-4.45	-6.34	-8.03
	2.94	11.77	10.52	8.35	16.01	22.03
c-C <sub>3</sub> H <sub>6</sub>	<b>-2.647</b>	<b>-8.96</b>	<b>-8.20</b>	<b>-6.66</b>	<b>-13.60</b>	<b>-17.26</b>
	3.96	17.70	16.86	14.54	22.86	28.98
	-3.67	-14.82	-13.25	-10.48	-19.97	-27.72



TABLE VIII. Anisotropic dispersion coefficients  $C_6''(A,B)$ . The results in this work are given in the first row. The second row gives the results corresponding to equations (12) and (24), while the third row corresponds to equation (22). For  $H_2$  an accurate theoretical value has been given in the fourth row (Ref. 28). The computational accuracy for our results is estimated to be 10% for  $c\text{-}C_3H_6$ , 5% for  $NH_3$ , and 2% for the other molecules.

	$H_2$	$N_2O$	$CO_2$	$NH_3$	$C_2H_6$	$c\text{-}C_3H_6$
$H_2$	<b>0.143</b>	<b>1.28</b>	<b>0.99</b>	<b>0.066</b>	<b>0.281</b>	<b>-0.282</b>
	0.13	1.02	0.79	-0.42	-0.04	0.27
	0.18	1.85	1.34	0.10	0.37	-0.46
	0.130	...	...	...	...	...
$N_2O$		<b>11.5</b>	<b>8.97</b>	<b>0.53</b>	<b>2.51</b>	<b>-2.49</b>
		8.83	6.62	-1.28	0.92	-0.69
		19.32	13.97	1.01	3.80	-4.79
$CO_2$			<b>7.01</b>	<b>0.376</b>	<b>1.95</b>	<b>-1.92</b>
			5.00	-1.34	0.48	-0.04
			10.10	0.73	2.75	-3.46
$NH_3$				<b>0.118</b>	<b>0.138</b>	<b>-0.173</b>
				4.58	2.27	-5.55
				0.05	0.20	-0.25
$C_2H_6$					<b>0.555</b>	<b>-0.559</b>
					1.43	-3.15
					0.76	-0.94
$c\text{-}C_3H_6$						<b>0.577</b>
						7.37
						1.19

results, while the third row refers to the results obtained with the approximate formula (21). The striking feature of this table is the disagreement between the values in the second row and the other values, where the anisotropy of  $NH_3$ ,  $C_2H_6$  or  $c\text{-}C_3H_6$  is concerned. Clearly, Hohm's fit describes the frequency-dependence of the polarizability anisotropies of these molecules incorrectly. This may be due to the fact that only a small number of data on the polarizability anisotropy were available (only for one frequency in the case of  $NH_3$ ), which may have caused erroneous fit parameters. There is qualitative agreement between our results and the traditional semi-empirical results in the third row. These semi-empirical results are generally higher than ours. In the cases where Hohm's results are close to the other results ( $H_2$ ,  $N_2O$  and  $CO_2$ ), his values are too low, as in Table VI.

In Table VIII the results for  $C_6''$  are presented. As in the previous table, the second row gives Hohm's own results, while the third row gives the results with equation (22). The results for  $C_6''$  in our table differ from those in Hohm's paper due to our use of the factor  $\frac{1}{6}$  in equation (22), while Hohm used  $\frac{1}{8}$  in his table.<sup>48</sup> The features of Table VII are magnified here. Hohm's results are unsatisfactory for  $NH_3$ ,  $C_2H_6$  and  $c\text{-}C_3H_6$ . The results in the third row are too large in absolute value. Hohm's results for  $H_2$ ,  $N_2O$  and  $CO_2$  are too small.

The approximation that the average polarizability and the polarizability anisotropy have the same frequency-dependence, which has implicitly been made in equations (21) and (22), is not always a good approximation. The overestimation in the results of Tables VII and VIII with the traditional semi-empirical formulas may be largely due to this approximation.

Table II gives an impression of the quality of our dispersion coefficients in Tables VI, VII and VIII. For example, the

polarizability anisotropy of  $NH_3$  is too high in Table II, which leads to the value of 0.118 in Table VIII. This value is too high. On the other hand, our static polarizability values for  $N_2O$  and  $CO_2$  are close to the experimental values, which suggests that the calculated dispersion coefficients are accurate for these molecules.

Summing up the results of Tables VI, VII, and VIII, we can say that our results always agree qualitatively with the traditional semi-empirical formulas. The results of Hohm's approach which involve the anisotropy of  $NH_3$ ,  $C_2H_6$  or  $c\text{-}C_3H_6$  are unsatisfactory. In the case of the other molecules ( $H_2$ ,  $N_2O$  and  $CO_2$ ), the situation is less clear cut, which seems to imply that the lack of data for  $\kappa(\omega)$  is mainly responsible for Hohm's erroneous results for the larger molecules. Our results involving anisotropies are always in between the two semi-empirical results. We believe that our own values are the most reliable ones.

## VII. CONCLUSIONS

An efficient way for calculating frequency-dependent polarizabilities and  $C_6$  Van der Waals dispersion coefficients has been implemented in the ADF program using the Adiabatic Local Density Approximation. The results involving average polarizabilities are of similar quality as TDCHF calculations. The isotropic dispersion coefficients show a clear tendency to be too large, due to the overestimation of  $\alpha_0$ . If polarizability anisotropies are concerned, our results compare favorably to both TDCHF and MBPT results. We used our results to compare two semi-empirical ways to calculate anisotropic Van der Waals dispersion coefficients.

The extension of the ALDA to arbitrary closed-shell molecules opens up the possibility to investigate molecular properties such as photoabsorption, frequency-dependent linear response and long-range Van der Waals interactions within DFT for general medium-sized molecules.

Extensions to non-local or frequency-dependent functionals and to frequency-dependent hyperpolarizabilities seem feasible.

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